

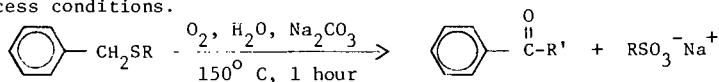
SYNTHETIC POLYMERS AS MODELS FOR COAL IN A DESULFURIZATION PROCESS

Thomas E. Schmidt, Thomas G. Squires and Clifford G. Venier

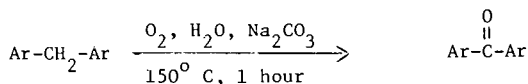
Ames Laboratory*, Iowa State University, Ames, Iowa 50011

Oxydesulfurization processes use air or oxygen to remove sulfur from coal for the purpose of converting high sulfur coal into an environmentally acceptable solid fuel (1). The desulfurization is mainly from the conversion of pyritic sulfur into sulfate and its removal when the coal is recovered from the aqueous slurry of the process (2). Because evidence for the removal of organic sulfur from coal could revitalize the now dormant status of oxydesulfurization as a method of coal beneficiation, we have been investigating the ability of these processes to degrade organic sulfur functions.

A direct comparison of a coal's organic sulfur content before and after process treatment is fraught with uncertainty due to the confusion in distinguishing the various forms of sulfur in coal (3). Therefore, our evaluation of the Ames Process, which employs oxygen and 0.2 M aqueous sodium carbonate at 200 psi total pressure and 150° C, has been based on the use of model compounds (4). In these investigations, the organic sulfur functional groups exhibited one of three kinds of behavior: direct autooxidation of the sulfur, indirect oxidation of the sulfur via autooxidation of an adjacent, benzylic C-H bond; and no reaction. Thiols and disulfides were directly oxidized to sulfonates which were stable under process conditions (i.e. no carbon-sulfur bond cleavage). Model compounds containing a benzylic sulfide function gave products (Equation 1) via a reaction pathway which is analogous to the autooxidation of benzylic C-H's in diarylmethanes (Equation 2). Other sulfides were recovered unchanged after one hour under Ames Process conditions.



R = methyl or phenyl, R' = H or OH



The further evaluation of the Ames Process with model compounds has been aimed at considering the relation between desulfurization and the autooxidative degradation of the substrate as a whole.

The evaluation of oxydesulfurization processes using simple model compounds is well suited for determining the reactivity of particular functional groups, but does not speak to effects on that reactivity when such are part of an extended hydrocarbon matrix. The influence of the proximate environment on the oxidation of sulfur functions is expected to be based on factors such as:

- 1) inhibition to mass transport of reagents or oxidation products;
- 2) competitive reactivity by hydrocarbon functions; and
- 3) intramolecular propagation of autooxidation.

In order to devise a model substrate for process evaluation in which sulfur is incorporated in a hydrocarbon matrix while maintaining the ability to describe the results in terms of functional group reactivity, we have prepared a series of synthetic polymers which meet the requirements outlined below :

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- 1) a high carbon, hydrogen and sulfur content,
- 2) a predictable average structure, and
- 3) sufficient crosslinking to impart insolubility.

Such polymers simulate some of the physical properties of coal and allow the recovery of the hydrocarbon content of the model as a solid product, which procedure is a basis of oxydesulfurization processes.

Materials

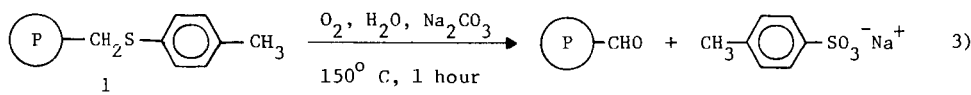
The modification, outlined in Figure 1, of chloromethylated polystyrene beads (Bio beads S-XL, 200-400 mesh, BioRad Laboratories, Richmond, CA) provides a convenient entry to several polymers meeting the above requirements as well as being comparable one with another. The preparation of a formaldehyde condensation polymer (Figure 2), which is closer than polystyrene to the H/C ratio of coals and is high in diarylmethane functions, was also carried out although this polymer is less defined as to its average size and structure. Similar condensation polymers, without sulfur, had previously been proposed as models for coal (5).

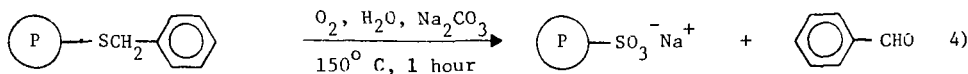
Experimental

The procedure by which the synthetic polymers were subjected to the Ames Process is described here. The dry polymer, 0.6 to 1.8 g, and 100 ml of 0.2 M aqueous sodium carbonate were placed in a 300 ml autoclave, which was flushed three times with nitrogen at 80 psi pressure, and the sealed autoclave was heated to the operating temperature. When the temperature had reached 150° C, oxygen was added to a total pressure of 200 psi and the autoclave was vented until the pressure was about 100 psi. The addition of oxygen was repeated twice, then the sealed autoclave was stirred at 1500 rpm for 1 h. while maintaining the temperature at 150 ± 10° C. In the case of these polymers, no significant amount of material was lost by the venting procedure. After cooling to room temperature the residual pressure (70 to 90 psi) was vented. The solid was collected by filtration, using 400 ml of distilled water to rinse the autoclave and wash the solid. The solid was successively washed with 30 ml portions of methanol, THF and benzene, then dried under reduced pressure and 80 to 90° C for at least five h. prior to weighing, recording the IR spectrum (KBr pellet) and submitting a sample for elemental analysis (elemental analyses were performed by Galbraith Laboratories, Knoxville, TN). The residue obtained by evaporation of the combined organic solvents exhibited PMR and IR spectra characteristic of polystyrene. In the case of (4-polystyryl)methyl 4-tolyl sulfide (1), sodium 4-toluenesulfonate in the residue of the aqueous phase was measured by its integral intensities in the PMR spectrum relative to *t*-BuOH as an internal standard. In the case of benzyl (4-polystyryl) sulfide (2), the aqueous phase was extracted with dichloromethane and benzaldehyde was found to be present in the extract in a yield of 19 % based on the amount of sulfur in 2.

Results

The effect of the Ames Process on the synthetic polymers was monitored by the degree of solubilization and the elemental analysis of the solid product. For polystyrenes, the formation of soluble polymers is a measure of the extent of autooxidation of the polystyryl backbone (6); this degradation will have no significant effect on the S/C ratio of the recovered solids. It is only when a C-S bond is more susceptible to autooxidative cleavage than the polymer backbone that a marked change in the S/C ratio can occur. This behavior is exhibited by polymers 1 (Table 1) and 2 (Table 2) which contain the benzylic sulfide function. The decrease in the S/C ratio in recovered polymer 1 and the increase in this ratio for recovered polymer 2 is explained by the facile autooxidation reactions shown in Equations 3 and 4.





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While the extent of desulfurization and polymer solubilization of 1 over four seemingly identical runs (Table 1) were quite variable, there is a correlation between the two types of degradation, i.e. more desulfurization was accompanied by more solubilization. That radical initiation of autoxidation is important for both processes was shown by the fact that the inclusion of a specific initiator, 2,2'-azobis (2-methylpropionitrile) (AIBN), increased both desulfurization and solubilization of polymer 1. In contrast, the use of AIBN with 2 was counter-productive with respect to desulfurization. This result is entirely consistent with our earlier findings that DBT is inert to Ames Process conditions and with our postulate that C-S bond cleavage must be initiated by autoxidation of an α -H.

When coal is subjected to an oxydesulfurization process, indigenous labile functions can presumably initiate autoxidation. It has been reported for example, that the pyridine soluble portion of coal contains substances which promote the air oxidation of coal at 100° C (7). To test whether a pyridine extract of coal could initiate the autoxidation of 1, we added such an extract to 1 under the conditions of the Ames Process. This result is reported in Table 1 and leads to the conclusion that the extract was not an effective initiator of autoxidation under these conditions.

Table 2 contains sulfur functions which are inert to the process conditions, i.e. DBT, DBTO₂ and ethyl phenyl sulfone; and, in these systems, autoxidation was not accompanied by desulfurization. This is especially evident with the condensation polymer 7, which is perhaps a better model for coal than polystyrene (8). The ability of the Ames Process to oxidize fluorene (4) suggested that 7 should undergo autoxidation. This was established on the basis of the degree of solubilization, the presence of carbonyl functions in the recovered solid (as detected by IR, 1715 cm⁻¹) and the incorporation of oxygen in the solid.

Conclusions

Although the Ames Process was designed to oxidize and remove sulfur from coal, these reaction conditions promote autoxidation of hydrocarbon functions as well, and the relative rates of hydrocarbon oxidation and organic sulfur removal are determined by the particular structure of each. Benzylic sulfides were the only case examined where C-S bond cleavage was significant precisely because of its greater susceptibility to autoxidation relative to the hydrocarbon part of the polymer. When incorporated into a hydrocarbon polymer, benzylic sulfides were found to be less reactive under the process conditions than the monomer benzyl phenyl sulfide (4). There is no indication that the hydroperoxides, which are formed by autoxidation of labile C-H bonds, react with sulfides to produce sulfoxides or sulfones under these conditions.

In this evaluation of the Ames Process with polymer models, we have shown that:

- 1) only benzylic sulfides undergo preferential C-S bond cleavage;
- 2) this cleavage is a radical process analogous to hydrocarbon autoxidation;
- 3) conditions which accelerate the oxidative cleavage of these C-S bonds will also increase the rate of degradation of the hydrocarbon matrix;
- 4) as expected, the rate of reaction of the benzylic C-S bond is attenuated when the sulfide is incorporated into an insoluble polymer.

Figure 1. Synthesis of Modified Polystyrenes for Use as Coal Models.

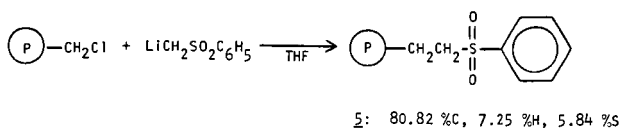
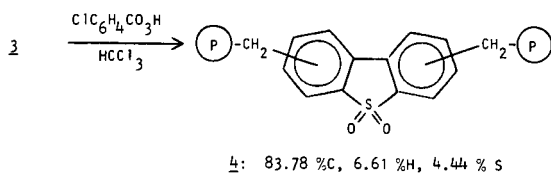
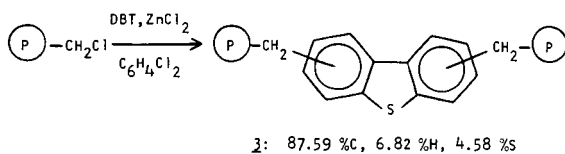
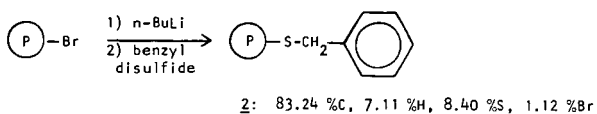
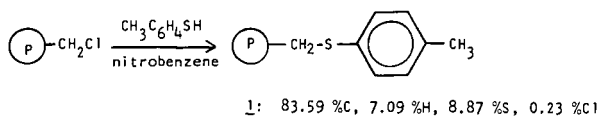


Figure 2. Hypothetical Structure for DBT/Fluorene/Formaldehyde Copolymer (7).

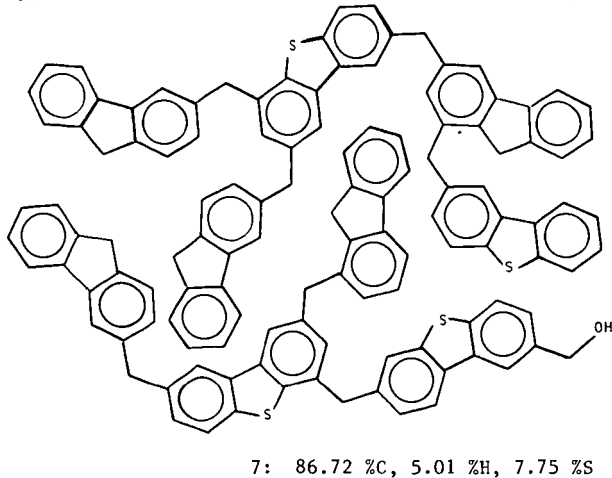


TABLE 1. Effect of Ames Process on (4-Polystyryl)methyl 4-Tolyl Sulfide (1).^a

Initial Wgt.	Recovered as a Solid ^b				% CH ₂ -S ^c Cleavage	4-Tolyl Sulfonate	Soluble ^d Polymer
	Weight	Carbon	Sulfur	ΔS/C			
0.91 g	84 %	81 %	57 %	-30 %	37 %	22 %	4.5 %
0.91	92	90	76	-16	21	28	2.7
1.14	93	91	76	-17	22	18	1.7
0.60	92	93	92	- 1	2	0.3	0
average of four	90	89	75	-16	20	17	2.2
1.00 ^e	89	88	76	-13	17		-
0.74 ^f	86	83	54	-34	42		9.3

TABLE 2. Effect of Ames Process on Some Synthetic Polymers.^a

Polymer	Initial Wgt.	Recovered as a Solid ^b				Soluble ^d Polymer
		Weight	Carbon	Sulfur	ΔS/C	
Polystyrene ^g	1.59 g	96 %	96 %	-	-	2.3 %
Polystyrene ^{g,h}	1.50	95	-	-	-	0.7
<u>2</u>	0.62	87	84	98 %	+17 %	3.2
<u>3</u>	0.78	96	96	97	+ 1	1.4
<u>4</u>	0.73	104	101	102	+ 1	1.0
<u>5</u>	1.16	94	95	96	+ 1½	0
<u>7</u>	1.06	89	87	88	+ 2	9.4
<u>7</u> ^f	0.90	95	92	95	+ 5	4.0

a) See Figures 1 and 2 for the structures of the polymers.

b) Presented as a percentage of the corresponding original values.

c) This is based on the loss of sulfur relative to the polystyryl carbon, which is the total carbon less the carbon due to the 4-tolyl groups, and is calculated as $100\% - 100\% \left(\frac{S_p C_i - 7S_p S_i}{S_i C_p - 7S_p S_i} \right)$ where S_p is the moles per unit weight of sulfur in the solid product, S_i is the moles of sulfur in the initial polymer, C_i is the moles of carbon in the initial polymer and C_p is the moles of carbon in the solid product.

d) Residue after evaporation of the organic solvents as a percentage of the initial weight.

e) Pyridine extract of an Ill. No. 6 coal, 0.1 g, was added to this run; the presence of the extract masked detection of soluble polymer.

f) With 0.16 g of AIBN added and oxygen added before heating the autoclave.

g) Biobeads S-X1, 200-400 mesh, prewashed with benzene and MeOH.

h) N₂ atmosphere only instead of O₂; elemental analysis not obtained.

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